Influence of Tillage, Cropping, and Nitrogen Source on the Chemical Characteristics of Humic Acid, Fulvic Acid, and Water-Soluble Soil Organic Matter Fractions of a Long-Term Cropping System Study

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Abstract: The characterization of organic matter in agroecosystems is important because of its involvement in many important soil ecosystem processes. Humic acid, fulvic acid, and water-extractable organic matter from a 9-year agroecosystem study investigating the effects of tillage, cropping system, and N source was characterized using multidimensional fluorescence spectroscopy with parallel factor analysis (PARAFAC). The fluorescence spectra suite containing all three types of organic matter fractions was modeled by five PARAFAC components. The distribution of component concentrations was unique to each type of organic matter fraction, indicating that these operational extracted fractions reflect differing chemical pools of soil organic matter. The three treatment factors (tillage, cropping, and N source) investigated in this study did not affect the component distribution of the humic and fulvic acid fractions that are regarded as the refractory pools of soil organic matter. In contrast, the component distribution of the more labile water-extractable organic matter fraction was significantly affected by the N source treatment. The results of this study support the use of multidimensional fluorescence spectroscopy with PARAFAC as a method to investigate how management practices of agroecosystems affect the dynamics and chemical nature of soil organic matter pools.

Key words: Humic substances, water-extractable organic matter, soil organic matter, multidimensional fluorescence spectroscopy, multiway analysis, PARAFAC.

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S oil organic matter is a heterogeneous mixture of complex geomolecules and biomolecules. Its involvement in important ecosystem processes such as plant nutrient availability, mineral weathering, and trace metal mobility and toxicity has led to extensive studies on the chemical nature of organic matter (Hering and Kraemer, 1998; Stevenson and Cole, 1999). Soil organic matter is formed from the decomposition of plant and animal matter (Kaiser and Guggenberger, 2000; Kögel-Knabner, 2002). Although organic matter consists of products along a decomposition continuum, it may be conceptualized as being composed of at least three distinct pools: an active labile pool with turnover times less than 1 year; an intermediate pool with

turnover times ranging from years to centuries; and a passive stable pool persistent in soils for thousands of years (Trumbore, 1997). The water-extractable organic matter (WEOM) fraction is the most labile and mobile fraction of the soil organic matter pool (Zsolnay, 1996). Chemical extraction approaches have been used to isolate differing fractions of soil organic matter. Strong base extractions have been used to extract humic acid (HA) and fulvic acid (FA) fractions from soils that are fractionated on their acid and base solubilities. Generally, FA has higher O and lower C content than HA, as well as higher acidic functional group content (Stevenson and Cole, 1999). Although a variety of protocols have been used to extract humic substances, the use of NaOH to extract the mixture of HA and FA from soils has been extensively used (Swift, 1996). The solution is acidified to precipitate the HA, and the supernatant containing the FA fraction is purified using hydrophobic resins.

Soil management practices such as tillage and crop rotations have been shown to affect total organic matter content and quality (Ohno et al., 2005; Sainju et al., 2008a). Tillage practices have also been shown to have differential effects dependent on the fraction of organic matter investigated. A long-term study found that bound amino acids in HA was higher for no-till soils compared with conventional till system, whereas FA-bound amino acids were higher in the conventional till system soils (Szajdak et al., 2003). Using discriminant analysis, Tatzber et al. (2008) demonstrated that the use of infrared and fluorescence spectroscopic analysis can satisfactorily separate soils into groups based on tillage and soil depth, indicating the ability of spectroscopic methods to follow organic matter dynamics. The HA fraction in a tropical cropping system study investigating tillage effects did not find treatment effects after 5 years using electron paramagnetic resonance, nuclear magnetic resonance, infrared, and fluorescence spectroscopy, which was attributed to the formation of clay-metal-organic matter complexes that protected the organic matter from microbial alterations (Gonzalez-Perez et al., 2004). The UV-visible absorption spectroscopy was used to show that organic matter under conventional tillage had lower quantities of low-molecular-weight humic substances compared with no-till tillage systems (MacHado and Gerzabek, 1993).

Fluorescence spectroscopy has been used to chemically characterize organic matter from terrestrial and aquatic sources because of its ability to distinguish different classes and provenance (Senesi, 1990; Stedmon et al., 2003). Parallel factor analysis (PARAFAC), a multiway statistical analysis, has been shown to decompose a suite of florescence excitation (EX)-emission (EM) matrices (EEM) into chemically meaningful spectral components (i.e., fluorophores) present in organic matter (Stedmon et al., 2003; Stedmon and Markager, 2005; Cory and McKnight, 2005; Ohno and Bro, 2006). A study comparing WEOM from plant biomass, animal manures, and soils reported that the components present were similar to the fluorescence spectral properties of

reference humic substances (Ohno and Bro, 2006). The similarities between the labile WEOM and the refractory humic substances are not expected because they have been traditionally seen to operationally fractionate soil organic matter into discrete and dissimilar categories. However, this similarity aligns with a new paradigm of humic substance structure proposed by Sutton and Sposito (2005), where humic materials are composed of low-molecular-weight components in associations through H-bonding and hydrophobic interactions. The presence of similar components in the labile WEOM and the refractory humic substances would be consistent with this new definition of humic substances.

With the recognition of soil organic matter for its critical role in issues related to ecosystem and agronomic sustainability, evaluating the effects of soil management on chemical characteristics of soil organic matter pools is needed to maintain and further enhance soil quality. A cropping system field study site to investigate the effects of tillage, crop rotations, and N source on cotton (*Gossypium hirsutum* L.) production in northern Alabama has been in place for 9 years (Sainju et al., 2008a, 2008b). This study has shown that greater residue production from the addition of N and cropping led to significant increases in soil organic carbon (SOC) concentration compared with a fallow treatment. Poultry litter addition increased the potential mineralizable and microbial biomass fractions of soil carbon compared with NH_4NO_3 additions (Sainju et al., 2008a). These results have shown that the rotation and N source treatments affected the biologically assayed SOC pools. Our goal in this study was to understand how the chemical characteristics of humic substances and WEOM were affected by different tillage, cropping management, and N source treatments using spectroscopic chemical assays.

MATERIALS AND METHODS

Soil Descriptions

The cropping system site is located at the Alabama Agricultural Experiment Station site in Belle Mina, and a detailed description of the study can be found in Sainju et al. (2008a, 2008b). The soil is classified as a Decatur silt loam (clayey, kaolinitic thermic, Typic Paleudults). The particle size distribu-

tion was sand, 150 g kg^{-1}; silt, 580 g kg^{-1}; and clay, 270 g kg^{-1}. The treatment management practices and selected chemical properties of the soils are described in Table 1. Briefly, treatments consisted of an incomplete factorial combination of tillage systems (conventional till, mulch till, and no-till), cropping system practices (cotton [*Gossypium hirsutum* L.]-cotton-corn [*Zea mays* L.] and rye [*Secale cereale* L.]/cotton-rye/cotton-corn), and N source (ammonium nitrate at 0 and 100 kg N ha^{-1} and poultry litter at 0, 100, and 200 kg N ha^{-1} application rates) treatments. The conventional tillage consisted of mold board plowing at 15- to 20-cm depth in November after autumn crop harvest and disking and leveling with a field cultivator in April before summer crop planting. Mulch tillage treatment used a rotary field cultivator to incorporate crop residue to depths of 5 to 7 cm before planting. No till operations involved planting using a no-till planter in undisturbed soil. The winter rye cover crop was planted in November and December at 60 kg ha^{-1} with a no-till driller without fertilization. Inorganic N fertilizer (NH_4NO_3) and poultry litter were broadcast 1 day before planting cotton in May. Both N fertilizer and poultry litter were incorporated to a depth of 5 to 8 cm in the conventional and mulch tillage and surface applied in no-till. The poultry litter applied in each year from 1997 to 2005 contained total C at 337 ± 22 g C kg^{-1} and total N at 33 ± 4 g N kg^{-1}.

Organic Matter Extractions

The International Humic Substance Society method was used on the soils for extraction of HA and FA (Swift, 1996). Briefly, the soil was extracted with 0.1 M NaOH, and the HA fraction was precipitated by acidification to pH 1 using 6 M HCl. The supernatant containing the FA fraction was purified by passing through columns containing DAX-8 resin and discarding the effluent. The FA was eluted off the column with 0.1 M NaOH and passed through H$^+$-saturated cation exchange resin to recover the H$^+$-saturated FA. Freeze-dried HA and FA samples were kept in a desiccator at room temperature. The WEOM fractions of the soils were extracted by adding 10.0 mL of deionized H$_2$O (DI-H$_2$O) to 1.00 g of soil in a 15-mL centrifuge tube. The suspensions were shaken on an orbital shaker for 30 min at room temperature (22 °C ± 1 °C), centrifuged at 900 g for 30 min, and filtered through 0.45-μm Acrodisk syringe filters.

TABLE 1. Description of Tillage, Cropping Management, N Source Treatments, and Selected Soil Chemical Characteristics of the Alabama Soil Set

Treatment	Tillage	Cropping System	N Source	N Rate, kg N ha^{-1}	Residue Biomass[†]	SOC, g C kg^{-1}	Total N, g C kg^{-1}
1	CT	Rye/cotton-rye/cotton-corn	None	0	54.8	12.9	1.53
2	CT	Cotton-cotton-corn	NH_4NO_3	100	104	15.2	1.75
3	NT	Cotton-cotton-corn	NH_4NO_3	100	117	13.5	1.20
4	CT	Rye/cotton-rye/cotton-corn	NH_4NO_3	100	126	14.3	1.88
5	CT	Rye/cotton-rye/cotton-corn	Poultry litter	100	110	18.3	2.03
6	MT	Rye/cotton-rye/cotton-corn	NH_4NO_3	100	126	15.9	1.96
7	MT	Rye/cotton-rye/cotton-corn	Poultry litter	100	106	15.4	1.39
8	NT	Rye/cotton-rye/cotton-corn	NH_4NO_3	100	148	13.5	2.16
9	NT	Rye/cotton-rye/cotton-corn	Poultry litter	100	120	16.0	1.98
10	NT	Cotton-cotton-corn	None	0	89.1	12.6	1.43
11	NT	Rye/cotton-rye/cotton-corn	Poultry litter	200	152	16.6	2.13
12	NT	Fallow	None	0	—	11.0	1.07

[†]From Sainju et al. (2008a).

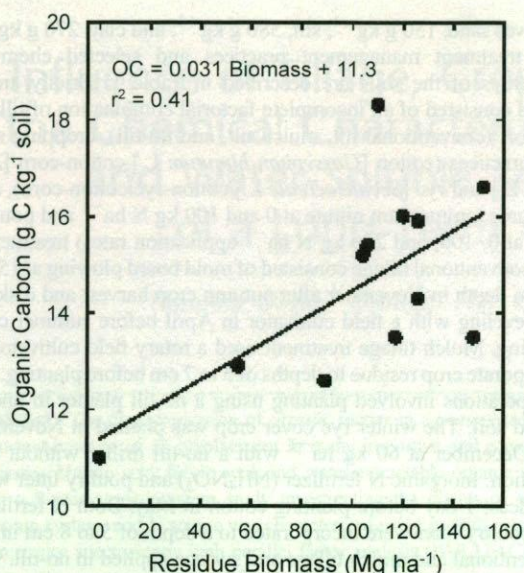CT: conventional till; MT: mulch till; NT: no-till.

FIG. 1. The SOC content of soils as a function of total residue biomass production from 1997–2005 in the cropping system study. The biomass data are from Sainju et al. (2008a).

The extraction period was selected to minimize WEOM microbial alteration during extraction (Zhou and Wong, 2000).

Fluorescence and PARAFAC Modeling

The WEOM extract was diluted with DI-H_2O to an absorbance value at 260 nm ($A_{260} \approx 0.1$). The HA and FA samples were dissolved in 0.05 M NaOH with 10 mg dry matter mL^{-1}. The HA and FA solutions were diluted to $A_{260} \approx 0.1$ with 50 mmol/L phosphate-borate buffer solution adjusted to pH values of 6, 7, and 9. There were no systematic differences in fluorescence landscape intensities between the three pH values so the three pH treatments were used as replicates for the fluorescence analysis. Fluorescence EEM spectra were obtained using a Hitachi F-4500 spectrofluorometer with an EX range set from 240 to 400 nm and

an EM range set from 300 to 500 nm in 3-nm increments. Instrumental parameters were EX and EM slits, 5 nm; response time, 8 sec; and a scan speed of 1200 nm min^{-1}. The PARAFAC modeling approach has been described in detail elsewhere (Andersen and Bro, 2003; Smilde et al., 2004), and only a brief description will be given here. Essentially, a PARAFAC model of a set of EEM spectra provides an estimate of the number of fluorophores as well as the EX and EM spectrum of these fluorophores. It also provides the relative concentration of each fluorophore in each sample. Each fluorescence landscape measurement provides an EEM, and when several of these are combined, they can be held in a three-way array of size $I \times J \times K$, where I is the number of samples, J the number of EM wavelengths, and K the number of EX wavelengths.

Such a three-way array cannot directly be modeled by standard multivariate analysis tools because these only work on two-way matrices. The PARAFAC model is specifically made to deal with such three-way data and can be viewed as an extension of principal component analysis (Harshman, 1970). Unlike principal component analysis, the PARAFAC model is uniquely identified without additional orthogonality constraints (Sidiropoulos and Bro, 2000). This means that if the underlying structure of the three-way data coincides with the PARAFAC model, then the parameters of the PARAFAC model will reflect the true underlying parameters. For fluorescence data, this is ideally the case, and each fluorophore will give rise to one PARAFAC component, and each such component consists of an estimated EM spectrum, an estimated EX spectrum, and a score vector where each element is the relative concentration of the fluorophore.

Before PARAFAC modeling, several preprocessing steps were used to minimize the influence of scatter lines and other attributes of the EEM landscape that are caused by the background solution matrix. Subtraction of a control DI-H_2O EEM from sample EEM was used to remove the lower intensity Raman scatter lines. The higher-intensity Rayleigh scatter line was removed by replacing the fluorescence intensity values with missing values in the region immediately adjacent to where EM wavelength was equal to one and two times the EX wavelength. In addition, the EEM spectra had a triangular-shaped region where the EM wavelength was less than that of the EX

TABLE 2. Pooled Tillage, Cropping Systems, and N Source Effects on the Biomass Production, Soil Carbon Content, and Soil N Content of the Alabama Soil Data Sets

Treatment	Biomass Production	SOC	Total N
Tillage			
CT	98.7 ± 30.7	15.2 ± 2.3	1.80 ± 0.21
NT	125 ± 25.6	13.9 ± 2.1	1.66 ± 0.49
MT	116 ± 14.1	15.7 ± 0.4	1.68 ± 0.40
Significance	NS	NS	NS
Cropping system			
Cotton-cotton-corn	103 ± 14	13.8 ± 1.3	1.46 ± 0.28
Rye/cotton-rye/cotton-corn	117 ± 30	15.4 ± 1.8	1.88 ± 0.27
Significance	NS	NS	NS
N source			
None	72.0 ± 24.3	12.2 ± 1.0	1.34 ± 0.24
NH_4NO_3	118 ± 10	14.5 ± 1.1	1.79 ± 0.36
Poultry litter	122 ± 21	16.6 ± 1.2	1.88 ± 0.33
Significance	None vs. NH_4NO_3 and litter*	None vs. NH_4NO_3 and litter; NH_4NO_3 vs. litter*	NS

*Significant at the 5% level.

CT: conventional till; MT: mulch till; NS: not significant; NT: no-till.

wavelength. Such a characteristic is a physical impossibility, and thus these data pairs were set to zero (Thygesen et al., 2006).

The PARAFAC modeling was conducted with MATLAB Release 14 (Mathworks, Natick, MA) using PLS_Toolbox version 4.0 (Eigenvector Research, Manson, WA). A nonnegativity constraint was applied to the parameters to allow only chemically relevant results. The PARAFAC models with two to six components were computed for the pooled HA, FA, and WEOM EEM. The determination of the correct number of components in the data set was assessed by the core consistency diagnostic score, which should be close to 100% for appropriate models. The core consistency provides an estimate of how well the model captures trilinear information and if the consistency turns low, that is, toward zero, it is a strong indication that the model is invalid (Bro and Kiers, 2003). The number of components was further validated by visual inspection of the estimated parameters and additional model diagnostics.

RESULTS AND DISCUSSION

Soil Chemical Properties

The annual addition of crop residue in the treatment plots where cropping was included during the 9-year period of this study increased the SOC content of the cropped treatments as compared with the fallow treatment (Table 1) (Sainju et al., 2008a). There was a significant linear regression relationship ($P = 0.026$) between biomass production and SOC, indicating that the building up of C stock in soils is directly proportional to the quantity of plant biomass input (Fig. 1). Because of the incomplete factorial design of the experiment (Table 1), the effects of tillage, cropping systems, and N source on biomass production, total organic carbon, and total N were evaluated by pooling treatments of the other two main factors. Statistical significance was evaluated using a t test of the means. In this cropping system study, there was no significant effect of tillage or cropping system on biomass production, SOC content, or total N content (Table 2). Addition of N, as either NH_4NO_3 or poultry litter, significantly increased the biomass production by 67% from 72 to 120 Mg ha^{-1}. This increase in biomass production resulted in a significant increase in SOC content (Table 2). Furthermore, there was a significant higher SOC content in the poultry litter treatment compared with the NH_4NO_3 treatment, which suggests that the poultry litter itself may contribute to increasing SOC buildup beyond its role as an N source for crop growth. Laboratory studies have shown that the WEOM fraction of poultry litter strongly adsorbs to soil mineral surfaces because of greater humification than the WEOM derived from plant biomass (Ohno et al., 2007). This greater sorption of poultry litter WEOM may provide protection from microbial decomposition, which could lead to greater sequestration of SOC in the poultry litter amendment treatments. Although the NH_4NO_3- and poultry litter–amended soils had greater total N content than the soils with no added N, the differences were not significantly different.

Fluorescence Characteristics

Along with treatment effects on SOC quantity, changes in the chemical characteristics of the organic matter may also impact important soil processes. Soil organic matter is composed of a complex mixture of molecules with an estimated 1% of the aromatic portion acting as fluorophores (Leenheer and Croué, 2003). Although only a small fraction of the organic matter is fluorescent, the fluorophores are very sensitive to its chemical structure and its surrounding chemical environment, which allows for the general characterization of the chemical
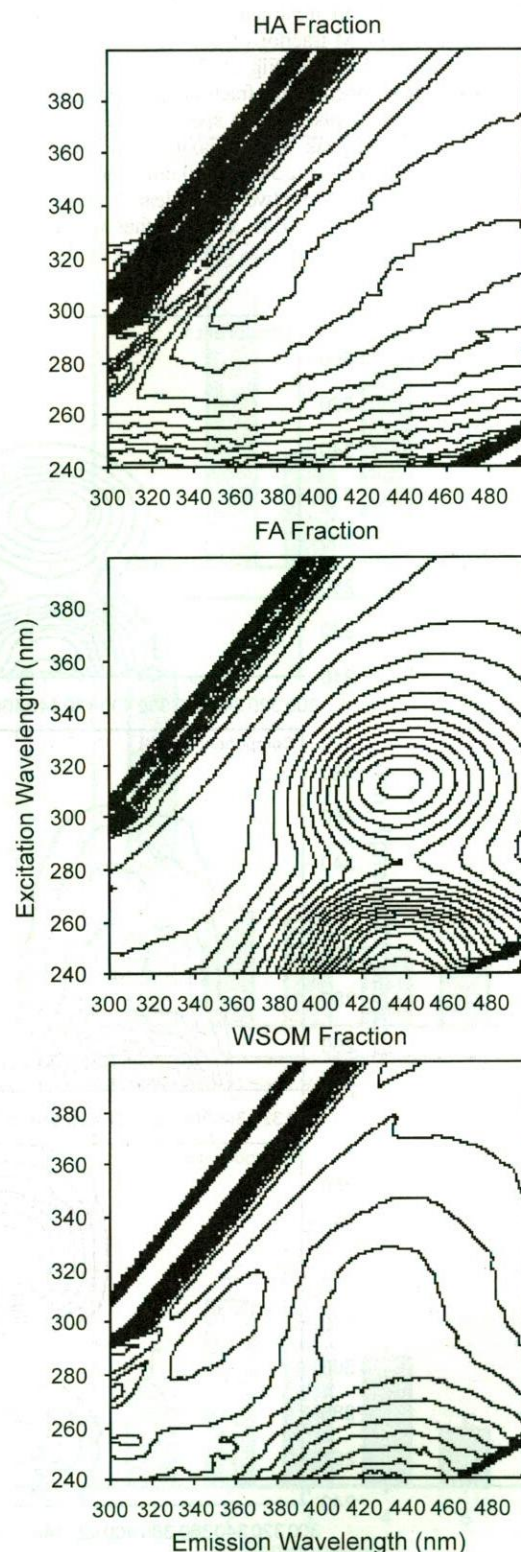

FIG. 2. The EEM fluorescence spectrum for the HA, FA, and water-soluble organic matter (WSOM) fractions of the no-till poultry litter (Treatment no. 9) soil.

nature of the organic matter present. The EEM spectra for the HA, FA, and WEOM fractions of the soils were visually distinctive between the three fractions but similar within the fractions among the 12 soil treatments. Representative EEM for the HA, FA, and WEOM fractions from the no-till poultry litter treatment no. 9 are shown in Fig. 2. The EEM were different, indicating that these operational fractions are representing dissimilar organic matter pools. The HA spectrum was characterized by a single very broad peak with a maxima at EX of less than 240 nm and EM maxima in the 300 to 460 nm region. In contrast, for the FA spectrum, there were two peaks clearly apparent, one at less than 240 nm EX/440 nm EM, and the other at 310 nm EX/ 440 nm EM. The former peak has been named as the A or α′

fluorophore, whereas the latter has been named as the C or α fluorophore (Stedmon et al., 2003; Sierra et al., 2005). The WEOM EEM spectrum was closer in visual appearance to the FA spectrum than the HA spectrum, with the 310 nm EX/440 nm EX being weaker in relative intensity than in the FA spectrum.

PARAFAC Analysis

To overcome the difficulty in interpreting broad and similar fluorescence EEM spectra, the EEMs from all of the treatments and fractions were combined for PARAFAC analysis, which can decompose EEM spectra into chemically meaningful components (Smilde et al., 2004). The PARAFAC models were computed, and the core consistency diagnostic scores were
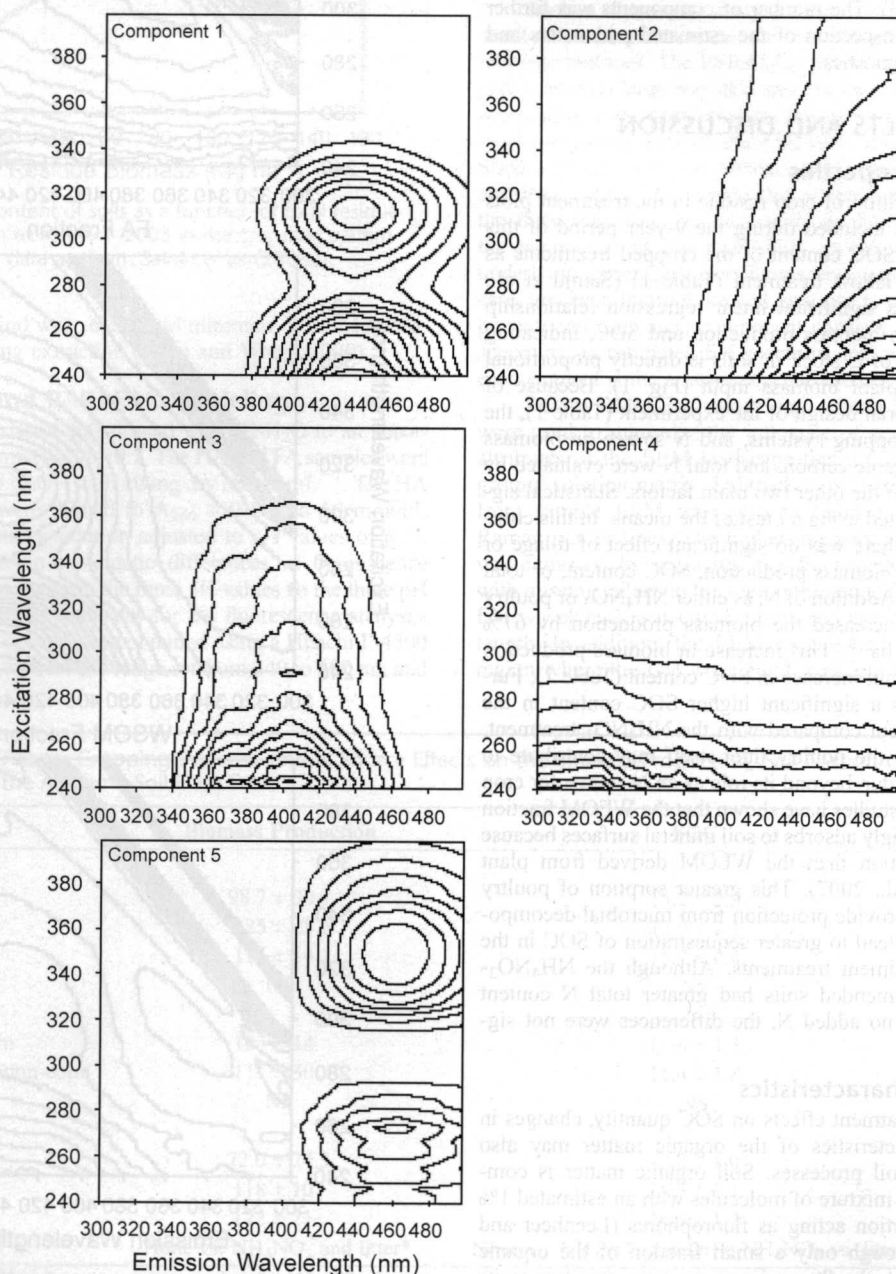

FIG. 3. The EEM spectral loadings of the five-component PARAFAC model of the HA, FA, and water-soluble organic matter fractions of soils from 12 treatments in the cropping system study.

99.8%, 99.6%, 96.7%, 99.7%, 77.5%, and 32.5%, respectively, for Components 2 to 7, indicating that the five-component model provided the greatest spectral resolution of the components and was likely to be the most appropriate model. Each fluorophore is represented by one PARAFAC component, and each component consists of a sample loading score holding relative concentrations, an EX loading representing the estimated EX spectrum, and an EM loading representing the EM spectrum. It is important to recognize that the concentrations are based on their fluorescence signal contributions that provide relative concentrations rather than their true chemical concentration contributions. Determination of the concentration score on a chemical concentration basis would require knowledge of the fluorescence quantum efficiencies of the individual components, which are currently unknown. The EEM spectra of each component obtained from fitting the five-component model to the EEM data suite are shown in Fig. 3.

Many studies have shown that organic matter derived from wide-ranging environments have qualitatively similar fluorescence components because of the presence of humic substances–like materials (Stedmon et al., 2003; Stedmon and Markager, 2005; Cory and McKnight, 2005; Sierra et al., 2005; Ohno and Bro, 2006). Components 1 and 5 have two EX spectral peaks and a single EM peak, which is a characteristic that has been widely reported with humic substances (Stedmon and Markager, 2005; Ohno and Bro, 2006). In addition, these two components have EX and EM spectra, which are similar to reduced quinone components observed by Cory and McKnight (2005) investigating aquatic natural organic matter. The spectral loadings of Component 2 resemble those of a component classified by Cory and McKnight (2005) as oxidized quinones. These reduction-oxidation status assignments are equivocal. A recent study by Macalady and Walton-Day (2009) have shown that the assignments as proposed by Cory and McKnight (2005) are not consistently indicative of the redox status of natural organic matter present in water or plant extracts. In addition, Ratasuk and Nanny (2007) have shown that the presence of redox-reversible quinones are present in both HA and FA. Component 3 is similar to a component also found by Cory and McKnight (2005), but is an unknown class of molecules (Cory and McKnight, 2005). This Component 3 was also reported to be present in WEOM extracted from soils, plant biomass, and animal manures (Ohno and Bro, 2006). Component 4 has its strongest EM in the 300 to 350, which is the region for amino acid–like components (Chen et al., 2003). The spectral loadings for Component 4 are similar to those of components considered amino acid–like by Cory and McKnight (2005).

Composition of Organic Matter Fractions

The fractional distribution of each component for the HA, FA, and WEOM pools averaged over all the soil treatments are shown in Fig. 4. Components 1, 2, 4, and 5 were found in the 13 International Humic Substances Society standard reference materials investigated; however, component 3 was not found in the study by He et al. (2008). This suggests that Component 3 is likely to be a water-soluble fraction of soil organic matter, and this is supported by this component being the dominant fraction in the WEOM extract (Fig. 4). The distribution of components in HA and FA pools were markedly different, with Component 1 being nearly absent for the HA but the dominant component in FA. About 80% of the fluorescence intensity was contributed by Components 2 and 4 in HA, whereas in FA, Component 1 contributed 50% of the fluorescence and the rest evenly distributed in the other components. The WEOM fraction also had significant contributions from all five components. Component 3

was present in the greatest concentration, contributing about a third of the fluorescence. Three components accounted for 97% of the fluorescence intensity for the HA pool, suggesting that it was the least complex in modeled fluorophore composition among the organic matter pools being investigated.
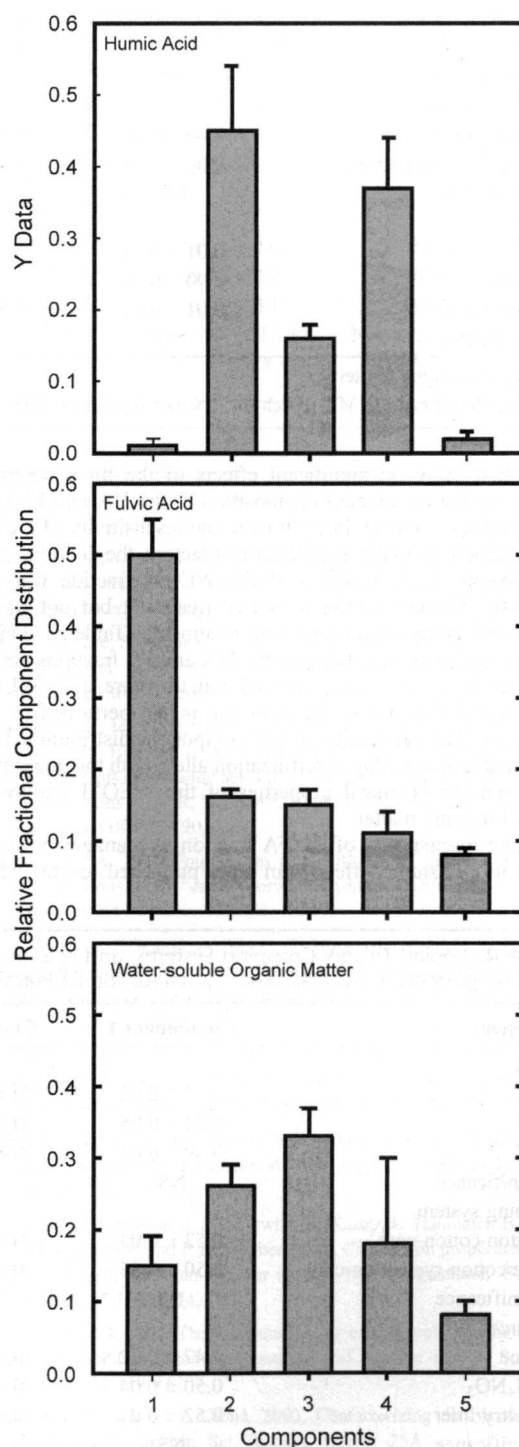

FIG. 4. Average relative fractional component distribution of the HA, FA, and water-soluble organic matter fractions for all 12 treatments in the cropping system study.

TABLE 3. Pooled Tillage, Cropping Systems, and N Source Effects on Relative Fractional Distribution of the Contents for the Five Components in the PARAFAC Model for the HA Fraction Extracted From the Alabama Soil Data Sets

Treatment	Component 1	Component 2	Component 3	Component 4	Component 5
Tillage
CT	0.01 ± 0.01	0.40 ± 0.04	0.17 ± 0.02	0.41 ± 0.03	0.02 ± 0.00
NT	0.01 ± 0.01	0.49 ± 0.10	0.16 ± 0.02	0.33 ± 0.09	0.02 ± 0.01
MT	0.00 ± 0.00	0.43 ± 0.01	0.17 ± 0.00	0.39 ± 0.00	0.02 ± 0.00
Significance	NS	NS	NS	NS	NS
Cropping system
Cotton-cotton-corn	0.00 ± 0.00	0.47 ± 0.07	0.16 ± 0.01	0.36 ± 0.06	0.01 ± 0.01
Rye/cotton-rye/cotton-corn	0.00 ± 0.01	0.45 ± 0.10	0.17 ± 0.02	0.36 ± 0.08	0.02 ± 0.02
Significance	NS	NS	NS	NS	NS
N source
None	0.01 ± 0.01	0.38 ± 0.02	0.18 ± 0.01	0.42 ± 0.01	0.02 ± 0.00
NH_4NO_3	0.00 ± 0.00	0.45 ± 0.06	0.16 ± 0.01	0.37 ± 0.04	0.02 ± 0.01
Poultry litter	0.01 ± 0.01	0.50 ± 0.12	0.16 ± 0.02	0.32 ± 0.11	0.02 ± 0.01
Significance	NS	NS	NS	NS	NS

Significant at the 5% level.

CT: conventional till; MT: mulch till; NS: not significant; NT: no-till.

There were no significant effects of the three treatment factors on the component composition of the HA and FA fractions (Tables 3 and 4). In contrast to the insensitivity of the HA and FA fractions to the three treatment factors, the distribution of Components 1, 2, 4, and 5 of the WEOM fraction was significantly affected by the N source treatment but not by the tillage and cropping management treatments (Table 5). This is perhaps not surprising because the HA and FA fractions are the more refractory fractions compared with the more labile WEOM fraction and likely to be the pool that is less perturbed by soil treatment. The sensitivity of the component distribution to N treatment indicates that N fertilization alters both the quantity of SOC and the chemical properties of the WEOM fraction of the soil organic matter.

The insensitivity of the FA fraction to management treatments in this study differs from other published results, where the FA fraction (Wander and Traina, 1996; Zalba and Quiroga, 1999) and HA fraction (Olk et al., 2000; Ding et al., 2006) of soil organic matter has been shown to be sensitive to management practices. A study using fluorescence and PARAFAC analysis to contrast WEOM spectra with those obtained from six terrestrial humic substances found that the humic substances–like components of WEOM were very similar in spectral properties to those obtained from the humic materials (Ohno and Bro, 2006). Kalbitz et al. (2003) used infrared spectroscopy, nuclear magnetic resonance spectroscopy, pyrolysis-field ionization mass spectrometry, as well as fluorescence EM spectroscopy to follow the dynamics of dissolved organic matter biodegradation. The four independent methodologies indicated the enrichment in monomeric lignin products with increasing biodegradation. These studies indicate that a variety of spectroscopic methods have the sensitivity to indicate structural

TABLE 4. Pooled Tillage, Cropping Systems, and N Source Effects on Relative Fractional Distribution of the Contents for the Five Components in the PARAFAC Model for the FA Fraction Extracted From the Alabama Soil Data Sets

Treatment	Component 1	Component 2	Component 3	Component 4	Component 5
Tillage
CT	0.47 ± 0.05	0.16 ± 0.00	0.16 ± 0.03	0.13 ± 0.02	0.08 ± 0.01
NT	0.53 ± 0.05	0.16 ± 0.00	0.14 ± 0.02	0.10 ± 0.04	0.08 ± 0.01
MT	0.49 ± 0.01	0.17 ± 0.01	0.16 ± 0.01	0.12 ± 0.01	0.08 ± 0.00
Significance	NS	NS	NS	NS	NS
Cropping system
Cotton-cotton-corn	0.53 ± 0.03	0.16 ± 0.00	0.13 ± 0.01	0.10 ± 0.03	0.08 ± 0.01
Rye/cotton-rye/cotton-corn	0.50 ± 0.05	0.16 ± 0.00	0.15 ± 0.02	0.11 ± 0.04	0.08 ± 0.01
Significance	NS	NS	NS	NS	NS
N source
None	0.47 ± 0.02	0.16 ± 0.00	0.16 ± 0.02	0.14 ± 0.04	0.07 ± 0.01
NH_4NO_3	0.50 ± 0.04	0.16 ± 0.00	0.14 ± 0.02	0.11 ± 0.02	0.08 ± 0.01
Poultry litter	0.52 ± 0.07	0.16 ± 0.01	0.14 ± 0.03	0.09 ± 0.05	0.08 ± 0.00
Significance	NS	NS	NS	NS	NS

Significant at the 5% level.

CT: conventional till; MT: mulch till; NS: not significant; NT: no-till.

TABLE 5. Pooled Tillage, Cropping Systems, and N Source Effects on Relative Fractional Distribution of the Contents for the Five Components in the PARAFAC Model for the WEOM Fraction Extracted From the Alabama Soil Data Sets

Treatment	Component 1	Component 2	Component 3	Component 4	Component 5
Tillage					
CT	0.14 ± 0.03	0.25 ± 0.03	0.30 ± 0.04	0.24 ± 0.10	0.07 ± 0.02
NT	0.16 ± 0.04	0.26 ± 0.04	0.34 ± 0.04	0.14 ± 0.15	0.09 ± 0.03
MT	0.17 ± 0.01	0.27 ± 0.00	0.33 ± 0.01	0.15 ± 0.02	0.09 ± 0.01
Significance	NS	NS	NS	NS	NS
Cropping system					
Cotton-cotton-corn	0.16 ± 0.03	0.25 ± 0.02	0.35 ± 0.05	0.15 ± 0.12	0.08 ± 0.02
Rye/cotton-rye/cotton-corn	0.16 ± 0.04	0.27 ± 0.03	0.32 ± 0.04	0.17 ± 0.13	0.09 ± 0.03
Significance	NS	NS	NS	NS	NS
N source					
None	0.11 ± 0.01	0.22 ± 0.02	0.29 ± 0.02	0.32 ± 0.04	0.06 ± 0.01
NH_4NO_3	0.16 ± 0.02	0.26 ± 0.02	0.34 ± 0.04	0.16 ± 0.09	0.08 ± 0.01
Poultry litter	0.18 ± 0.03	0.29 ± 0.02	0.34 ± 0.04	0.09 ± 0.10	0.11 ± 0.02
Significance	None vs. NH_4NO_3 and poultry litter*	None vs. NH_4NO_3 and poultry litter*	NS	None vs. NH_4NO_3 and poultry litter*	None vs. NH_4NO_3 and poultry litter; NH_4NO_3 vs. poultry litter*

*Significant at the 5% level.
CT: conventional till; MT: mulch till; NS: not significant; NT: no-till.

changes in water-extractable and the traditional base-extractable organic matter fractions as a result of experimental soil management treatments.

CONCLUSIONS

This laboratory study has clearly demonstrated that EEM fluorescence spectroscopy with PARAFAC is a rapid and sensitive method that is capable of monitoring the chemical characteristics of soil organic matter. The results indicate that the HA and FA fractions were not significantly affected by tillage, cropping, or N source treatments for this cropping system study. However, the chemical composition of the labile WEOM was affected by the N treatment, indicating that this more labile fraction of organic matter may be more affected by management treatment effects. This finding is significant and suggests that the WEOM fraction of soil organic matter should also be investigated to assess how soil management effects affect the chemical nature of soil organic matter.

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